

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO ELECTRICALLY CONDUCTIVE LAYERS PRODUCED BY PLASMA SPRAYING

(71) We, UNITED KINGDOM ATOMIC ENERGY AUTHORITY, London, a British Authority do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

5 This invention relates to a method of depositing a layer of material onto a substrate by plasma spraying, and to articles having such layers thereon.

In plasma spraying, an arc is struck between two electrodes, one of which is the spray nozzle, to generate a plasma in a high flowing, selected gas (e.g. hydrogen), and the material to be plasma sprayed is fed through the plasma, the 3MB system supplied by 10 Metco, Chobham, Surrey, being one example of a plasma spray system.

15 According to the present invention, there is provided a method of depositing a layer comprising titania having a predetermined electrical resistivity on to a substrate adapted to receive the titania, the method comprising heating the substrate, feeding particulate titania through a plasma adapted to cause a partial reduction of said titania, directing the partially reduced titania onto the substrate, and allowing the substrate and the titania thereon to cool in a controlled manner.

The substrate may be provided by an electrical insulating material.

Desirably, the method includes subsequently plasma spraying or flame spraying a metallic layer on a portion of said titania layer for electrical connection to an electric circuit. 20 By changing one or more of the parameters of the plasma spray conditions, or of the substrate, changes in the electrical resistivity of the deposited layer of titania can be introduced.

25 The plasma may be arranged to extend substantially to the substrate, and other parameters of the plasma spray conditions which might be changed to assist in bringing the required electrical resistivity in the titania layer include, residence time of the particulate titania in the plasma, the plasma producing gas, the gas for injecting the particulate titania into the plasma, and the spray distance.

It will also be understood that the invention includes an article having thereon a layer of titania having a predetermined electrical resistivity in a particular direction, which layer has 30 been deposited by the method of the invention.

A reducing environment may be provided about the substrate for example, by directing the flow of a reducing gas, which may be the plasma gas, across the substrate.

The electrical conductivity of the titania layer may be reduced by mixing an inert material such as alumina with the particulate titania, and plasma-spraying said mixture.

35 The predetermined electrical resistivity may be in a direction parallel to the titania layer, or normal to said titania layer.

The method of the invention will now be described by way of example only with reference to Examples in which the parameters of the plasma spray conditions, or of the substrate, were changed to effect a change in electrical resistivity of a titania layer.

40 In the following Examples mild steel substrates were degreased and grit blasted, and then heated and plasma sprayed in a furnace in an argon atmosphere, and subsequently allowed to cool in the furnace. Titania powder of 10 to 53 µm particle size and 99% + purity (Metco No (Registered Trade Mark) 102) was plasma-sprayed onto the substrates using a Metco No 3MB plasma-spray system and 3MP Powder Feed Unit to form a layer of titania 0.1-0.2 mm thick. Some of the parameters of the plasma-spray system or of the substrates were changed 45

for each substrate to provide titania layers on the substrates having different electrical resistivities.

Example I

5	Plasma Gas	-- N ₂ /H ₂ at gas pressures of 50 psi and gas flow rates in the ratio of 75:15 respectively	5
10	Powder Carrier Gas	- N ₂	10
	Substrate Temperature	- 238°C	
15	Powder Port	- No 2	15
	Arc voltage	- 75 volts	
	Arc current	- 500 amps	
20	Spray rate	- 8.1 lb/hour	20
	Spray distance	- 4 inches	
25	Resistivity (normal to the layer) - 4.9 × 10 ² ohm/cm		25

Example II

Example I was repeated but with the substrate temperature at 510°C, and provided a titania layer having a resistivity (normal to the layer) of 11.5 × 10³ ohm/cm

30	<i>Example III</i>		30
35	Plasma Gas	- A/H ₂ at gas pressures of 100 psi and 50 psi respectively, and gas flow rates in the ratio of 80 : 4 respectively	35
	Powder Carrier Gas	- O ₂	
40	Substrate Temperature	- 168°C	40
	Powder Port	- No 2	
	Arc voltage	- 47 volts	
45	Arc current	- 400 amps	45
	Spray rate	- 8.1 lb/hour	
50	Spray distance	- 4 inches	50
	Resistivity (normal to the layer) - 12.6 × 10 ³ ohm/cm		

Example IV

Example III was repeated but with the substrate temperature at 316°C, and provided a titania layer having a resistivity (normal to the layer) of 16.8 × 10³ ohm/cm

Example V

Example III was repeated but with the substrate temperature at 590°C, and provided a titania layer having a resistivity (normal to the layer) of 18.1 × 10⁶ ohm/cm.
In order to reduce the contact resistance between the titania layer and an electric circuit for measuring the resistivity of the titania layers in the above Examples, a metallic layer (e.g. 003") of copper or silver was deposited by a plasma spray or flame spray process over those portions of the titania layer at which electrical contact was to be made with the circuit, and such metallic layers are desirable in practical applications of the invention for

electrically connecting the titania layer to an electric component.

Although the electrical properties of the titania are changed after passage through the plasma, in this partially reduced state the titania still exhibited many of the properties of stoichiometric titania such as low thermal conductivity.

5 A material, for example, an inert material such as alumina may be mixed with the particulate titania and plasma-sprayed therewith to increase the electrical resistance of the titania layer to some required value, or to change other properties such as hardness or chemical properties. Alternatively, the titania may be pre-reacted instead of mixed with such a material.

10 Alternative substrates may be used, for example metals such as aluminium and molybdenum, and ceramics such as alumina. The titania layer deposited by the method of the invention should not be used as an electrical conductor at a temperature above about 500°C since the titania would rapidly oxidise and revert to its more natural conditions of an electrical insulator.

15 A stream of reducing gas, such as the nitrogen/hydrogen plasma gas, may be directed on to the substrate to inhibit any tendency there might be for the titania to oxidise as it cools on the substrate.

20 By suitable selection of the particle size of the titania and any inert filler used, a layer having a required permeability may be obtained, a more permeable structure resulting from increasing particle size.

The pressure of the plasma gas may be adjusted to suit any non-oxidising gas mixed with the plasma gas, for example, to produce a laminar flow when nitrogen is used but a turbulent flow with helium.

WHAT WE CLAIM IS:-

25 1. A method of depositing a layer comprising titania having a predetermined electrical resistivity in a particular direction on to a substrate adapted to receive the titania, the method comprising heating the substrate, feeding particulate titania through a plasma adapted to cause a partial reduction of said titania, directing the partially reduced titania onto the substrate, and allowing the substrate and the titania thereon to cool in a controlled manner.

30 2. A method as claimed in Claim 1, wherein the substrate is provided by an electrical insulating material.

35 3. A method as claimed in Claim 1 or Claim 2, including subsequently plasma spraying or flame spraying a metallic layer on a portion of said titania layer for electrical connection to an electric circuit.

40 4. A method as claimed in any one of the preceding Claims, wherein the plasma is provided substantially by nitrogen gas.

5. A method as claimed in any one of Claims 1 to 3, wherein the plasma is provided by argon and hydrogen gases at flow rates in the ratio of approximately 20:1.

45 6. A method as claimed in Claim 5, wherein the particulate titania is injected into the plasma by a gas comprising oxygen.

7. A method as claimed in any one of the preceding Claims, wherein the substrate and the plasma are at a distance therebetween such as to minimise re-oxidation of said partially reduced titania.

50 8. A method as claimed in any one of Claims 1 to 6, wherein the plasma extends substantially to the substrate.

9. A method as claimed in any one of the preceding Claims, wherein said substrate is situated in a furnace, and said substrate and the titania layer thereon are allowed to cool in said furnace.

55 10. A method as claimed in any one of the preceding Claims, wherein the plasma is produced by an arc voltage of between 47 - 60 volts and an arc current of about 400 amps.

11. A method as claimed in any one of the Claims, wherein the residence time of the particulate titania in the plasma is selected to provide a predetermined partial reduction of said titania.

55 12. A method as claimed in any one of the preceding Claims, wherein the predetermined resistivity is in a direction normal to the surface of said layer.

13. A method of depositing by plasma spraying a titania layer onto a substrate, substantially as hereinbefore described with reference to any one of the Examples 1 to 5.

14. An article having thereon a layer of titania having a predetermined electrical resistivity in a particular direction, which layer has been deposited by the method as claimed in any one of Claims 1 to 13.

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